

MEMO
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cc:

Mr. L. Klein

Date April 25, 1966

To Mr. G. Trout
Whitmoyer

From D. J. Butterbaugh

DATE STAMP

Subject: Waste Problem at Myerstown

Attached herewith is a copy of Dr. Kunin's memorandum No. RK-1008, Mr. Iezzi's memorandum to Mr. Geniesse dated April 21, as well as Mr. Graham's report, including his recommendations for additional wells and water treatment at Myerstown.

We expect to seek Mr. Graham's comments and advice on Dr. Kunin's work and preparation for a test on soil at Myerstown.



D. J. Butterbaugh

DJB/epb
attac.

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Mr. L. Klein
Dr. C. H. McBurney

Mr. T. Iezzi
Mr. F. J. Rarig
Dr. R. M. Ross

Bridesburg, April 21, 1966

Memorandum No. RK-1008

To: Dr. D. J. Butterbaugh (3)✓
From: R. Kunin (2)
Subject: Arsenic Waste Problem (Whitmoyer Laboratories)

As a result of our recent discussions on the persisting arsenic problem at Whitmoyer Laboratories, it was decided that we should explore the possibility of immobilizing the arsenic residues now present in the soil of the Whitmoyer property and perhaps that land adjacent to it. Since the arsenic residues now present in the soil may be the prime factor controlling the rate in which arsenic is now appearing in the ground waters, it may well be that centuries of pumping and precipitation may be required before the levels in the ground water are reduced to satisfactory levels. It has been reasoned that immobilization of the arsenic in the soil as an insoluble precipitate might reduce or eliminate the time-consuming and costly pumping operation.

With the above objective in mind, Research undertook the assignment to investigate the possibility of applying ferric sulfate directly to the soil in order to immobilize the arsenic. It is important to compare the rationale of this proposed procedure with that which is now being practiced at Whitmoyer. At present, we are pumping ground water and precipitating the arsenic with ferric sulfate and lime. The slurry is then lagooned on our property. The proposed soil treatment involves exactly the same chemistry. Ferric sulfate will be either injected or "drilled" into the soil and neutralized by the limestone now present in the soil or by the addition of lime, limestone, or ammonia. In both instances, we are immobilizing the arsenic as the identical chemical compound. In one case, the precipitate is being stored on the ground and, in the other case, in the ground.

If much of the arsenic that remains on the property is within the soil profile, it is quite logical to expect that, from purely a hydraulic viewpoint, pumping and treating the ground water is an impractical procedure if one expects to remove this arsenic within a reasonable period of time. The arsenical wastes in the soil are probably present as compounds that are not too soluble but sufficiently soluble to yield objectionable quantities of soluble arsenic. Because

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of this condition, one cannot depend upon rainfall as a means for naturally removing the arsenic now remaining in the soil. If the arsenic cannot be removed readily in this manner, it then becomes apparent that a means for immobilizing the arsenic in the soil must be considered.

The experimental study was divided into three phases: (1) prior evaluation of soil profile, (2) soil treatment, and (3) re-evaluation of treated soils.

I. Experimental Study

A. Prior Evaluation of Soil Profile

At our request, Mr. Trout of Whitmoyer Laboratories obtained four soil profile samples from the Whitmoyer property and the areas adjacent to it. The samples were taken almost to the depth of the bed rock. The sample descriptions and locations are given in Table 1 and Figure I.

Table 1

Description of Soil Profiles

Location	Sample No.	Depth of Sample
A. DDAA storage area, S.W. corner of Whitmoyer Property	4	Top Soil
	5	3 ft. below Surface
	6	6 ft. below Surface
B. Canal bank, near Well #6, 75 ft. west of pump house, north side of canal.	1	Surface Soil
	2	2 ft. below Surface
	3	5-6 ft. below Surface
C. Winthrop Property, 40 ft. west of C-6	7	Surface Soil
	8	2 ft. below Surface
	9	5-6 ft. below Surface
D. Weeping site near Grumbine house, 20 ft. north of Tulpehocken Creek	10	Surface Soil
	11	2 ft. below Surface
	12	3 ft. below Surface

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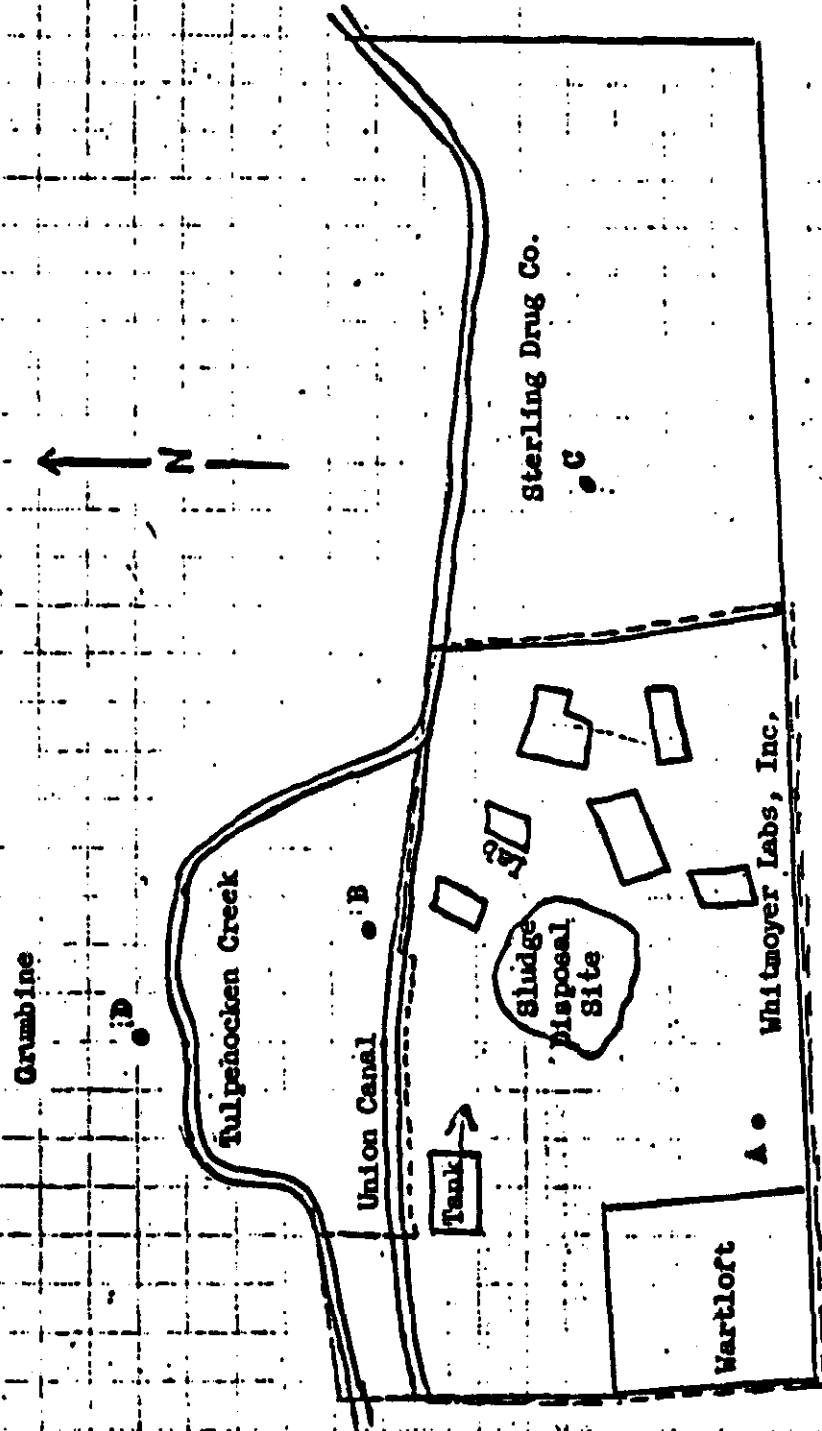


Figure I - Diagram of Whitmoyer Property and Location of Soil Profile Samples

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The soil samples were mixed to obtain uniform samples and analyzed for total arsenic by first digesting 25 grams in an excess of 6N sulfuric acid. The arsenic was then distilled as AsCl_3 and titrated with I_2 . Soluble arsenic was determined by extracting 200 grams of soil with 200 ml. of water and analyzing the extract by the AsCl_3 distillation procedure. Both of these analyses are quite time consuming but unavoidable considering the many potential interferences present in the soil. At least two to three days are required for an analysis of a soil sample. The procedures are, however, quite reliable. It must also be noted that sampling procedures are subject to some difficulties and may give rise to some minor errors. The data for these analyses are summarized in Table 2.

Table 2

Total and Soluble As Contents of Whitmoyer Soil Profiles

Sample No.	Location	Total As		Soluble As ^a	Soil pH
		%	lbs/acre-ft. ^b	ppm	
1	B-North	0.057	1140	25	7.2
2	side of	0.153	3060	55	7.5
3	Canal bank	0.165	3300	85	7.4
4	A-DDAA	0.300	6000	515	6.2
5	Storage	0.050	990	70	7.2
6	Area	0.044	870	175	7.7
7	C-Winth-	0.062	1230	8	7.8
8	rop Prop-	0.057	1140	8	7.5
9	erty	0.050	990	5	7.9
10	D-Grum-	0.006	120	5	7.1
11	bine Prop-	0.020	390	5	7.6
12	erty	0.029	570	5	7.5

^a 1-1 extract of soil sample.

^b 2,000,000 lbs. of soil = 1 acre-foot.

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7 It is quite evident that there is a considerable amount of arsenic throughout the entire soil profile on the Whitmoyer property and the land adjacent to it. Although the solubility data may indicate the arsenic present in the soil to be of limited solubility, subsequent tests show that the data represent a saturated solution and that these solubility values will persist even after several water extractions. The data of Table 2 indicate the surface layer of the old DDAA storage area to be most heavily contaminated; however, appreciable contamination appears throughout the entire profile of areas on the opposite side of the abandoned canal. One might interpret the data as indicating that the contamination of the area north of the canal originated from the lower depths upwards towards the surface. In other words, arsenic may have leached from the Whitmoyer soil, passed under the canal area, and rose upward in the soil north of the canal. This pattern does not appear to be the case with respect to movement towards the Winthrop property.

The data also indicate that there appears to be some variability in solubility of the arsenic in going from one profile to another. In particular, it appears that the As in the areas more distant from the Whitmoyer property is less soluble. This would indicate that the arsenic in these areas has been "fixed" by the soil. This could arise as a result of the naturally occurring iron in the soil, adsorption on the clay complex, or immobilized within the cell structure of microorganisms. Of course, As "fixing" capacity of the soil is limited and As fixation appears evident in those profiles low in As. One might estimate that the soil has a natural As fixation capacity of at least 500 lbs. per acre-foot.

It would be of considerable interest to estimate the total quantity of As present in the soil profile of the Whitmoyer property and the land adjacent to it. Unfortunately, the extent of sampling is such that only a very approximate estimate can be made. On the basis of the data reported in Table 2, one might assign an average value of 1500 lbs. of As per acre-foot to the Whitmoyer property and this would correspond to 9000 lbs. per acre assuming a six foot profile. Since the effective property is approximately 20 acres, one could conclude that 180,000 lbs. of As is in the soil profile on just the Whitmoyer property. An equal amount might also be assigned to both the area just north of the canal and to the Winthrop area. This is quite speculative because of the limiting sampling. It would not be unreasonable, however, to speculate that somewhere between 250,000 and 500,000 lbs. of As may reside in the soil profile on or about the Whitmoyer property.

B. Soil Treatment

Because of the limited (but appreciable from a health viewpoint) solubility of the As in the soil profile, it is quite difficult to see how one can reasonably expect to recover most of the arsenic by our current procedure which depends upon the natural leaching of arsenic from the soil into the ground water and pumping and treating such water. Because of this situation, it was considered advisable to investigate the possibility of treating the arsenic present directly in the soil with ferric sulfate.

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Samples of soil were first treated with a ferric sulfate solution and permitted to stand for four hours in order to permit the arsenic compounds to be contacted by the iron solution. The pH's of the soil suspensions were then measured and the suspensions were neutralized with lime to approximately pH 6 when necessary. The suspensions were then filtered at a ratio of 1-1 and the arsenic present in the filtrate measured as before. A comparison was made with samples of soil only treated with water. A series of runs was first made in which ferric sulfate was applied at a rate of 10 tons per acre-foot. According to our previous studies, this should immobilize those soils containing as much as 4000 lbs. As per acre-foot. The results of these tests are summarized in Table 3.

Table 3

Fe₂(SO₄)₃ Treatment of As Contaminated Soils

(Ten Tons Applied per Acre-Foot)

Sample No.	Location	Soluble Arsenic, ppm		pH Prior to Neutralization
		Before Treatment	After Treatment	
1	B	25	4	6.4
2	B	55	8	4.9
3	B	85	5	4.2
4	A	515	38	2.9
5	A	70	5	2.9
6	A	175	5	2.9
7	C	8	nil	6.3
8	C	8	nil	6.4
9	C	5	nil	6.4
10	D	5	nil	6.5
11	D	5	nil	6.3
12	D	5	nil	6.4

It is quite evident that the treatment is quite effective for all samples. One might conclude that more ferric sulfate should have been applied to Sample 4 whose arsenic content was 6000 lbs. per acre-foot. It is also quite possible that excessive quantities were applied to the other samples. It was noted above that this application rate should take care of contamination levels up to 4000 lbs. As per acre-foot.

It is interesting to note from the pH data of Table 3 that, except for Samples 4 and 5, no liming is really necessary even following the 10 ton per acre-foot application of Fe₂(SO₄)₃. This lack of need for liming is a result of the limestone nature of the soil.

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C. Evaluation of Treated Soils

In order to investigate the effect of the ferric sulfate application rate and the lasting effect of the treatment, two samples were studied at different application rates and the lasting effect of the treatment was studied by repeatedly extracting the treated soil with water. The data for these experiments are summarized in Table 4. It is quite apparent from these data that the ferric sulfate treatment has a lasting effect and that except for the very heavily contaminated area, application rates considerably below 10 tons per acre-foot is adequate. It would appear that since some of the arsenic is already possibly fixed, an application rate of 1 ton per acre-foot would be adequate for those areas having less than 1000 lbs. of As per acre-foot.

Table 4

 $\text{Fe}_2(\text{SO}_4)_3$ Treatment of As Contaminated Soils

Soil Sample	Location	$\text{Fe}_2(\text{SO}_4)_3$ Application Rate lbs/acre-foot	Soluble As, ppm			
			Before Treatment	After Treatment		
				1st Extract	2nd Extract	3rd Extract
1	B	10	25	2	1	1
1	B	5	25	2	1	1
4	A	20	515	38	50	50
4	A	10	515	10	10	8

II. Discussion

The most significant aspect of this work is the fact that a considerable amount of arsenic persists in the soil profile of the Whitmoyer property and the land adjacent to it. Although the arsenic is present as a slightly soluble material, the solubility is such that rain water leaching through the soil can result in objectionable concentrations of As appearing in the ground waters. It is quite apparent that our current practice of pumping and precipitation with iron will not remove this arsenic within a reasonable period of time.

Since the safety of the iron-arsenic precipitate has been established and accepted by the State authorities, it would be reasonable, at the present time, to consider the direct application of $\text{Fe}_2(\text{SO}_4)_3$ to the soil profile in order to immobilize or "fix" the arsenic that now persists throughout the soil profile. From a technical point of view, the problem does not pose any real difficulties. If one assumes the maximum amount of arsenic present to be 500,000 lbs., a maximum of 750 tons of $\text{Fe}_2(\text{SO}_4)_3$ may be required. At the current price of \$48 per ton,

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this would cost \$36,000; however, since some of the arsenic is already "fixed," the amount required will probably be 1/4 of this. Because of the limestone present in the soil profile, no liming agent will be required.

I cannot foresee any possible risk in undertaking the above procedure. I am attaching a previous memorandum (RK-852, March 26, 1965) which cites agricultural precedence for this method of soil treatment.

The only possible adverse consequences of the above procedure would be: (1) the acidic $\text{Fe}_2(\text{SO}_4)_3$ might solubilize a large amount of arsenic and set it "loose" into the ground water, (2) some injury to vegetation might occur with high applications of $\text{Fe}_2(\text{SO}_4)_3$, and (3) the $\text{Fe}_2(\text{SO}_4)_3$ might result in the formation of "red water" in the nearby streams or wells. I would rule out the first possible objection because of the limestone present in the soil and the bed rock. Any arsenic set free by the $\text{Fe}_2(\text{SO}_4)_3$ would not travel very far before it would precipitate. I would also rule out the second objection because of the fact that the highest application rate of ferric sulfate considered (10 tons per acre-foot) is not excessive for the soils involved. Finally, the ferric sulfate reaction results in a well coagulated precipitate which is not readily dispersed and therefore "red water" should not occur.

III. Recommendations

Although I feel that we should consider using the ferric sulfate soil treatment at Whitmoyer as soon as possible, we should, perhaps, discuss the matter first with our consultant, Mr. Graham, who expressed some interest in the method a few months ago. I should also like to suggest that we consider discussing the matter with Prof. Louis Kardos of Penn State University who has had some experience, I believe, in reclaiming arsenic contaminated soils with iron salts. If we receive some encouragement from these consultants, I further suggest that we experiment with the procedure on a small scale treating an acre of the highly contaminated soil and an acre of the slightly contaminated soil and then re-evaluate the soil profiles after the treatment according to the procedure described in this memorandum.

Robert Kunin

Robert Kunin

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